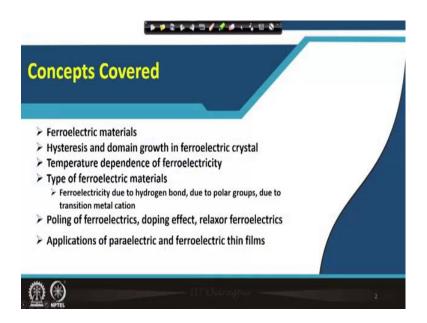
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Module - 05 Electrical, magnetic and thermal properties of non - metallic materials Lecture - 24 Ferroelectric behavior of non - metallic materials and ferroelectric thin film for non - volatile memory applications

Welcome to my course Non – Metallic Materials. And we are in module number 5, Electrical, magnetic and thermal properties of non–metallic materials. And this is lecture number 24, Ferroelectric behavior of non–metallic materials and ferroelectric thin film for non–volatile memory applications.

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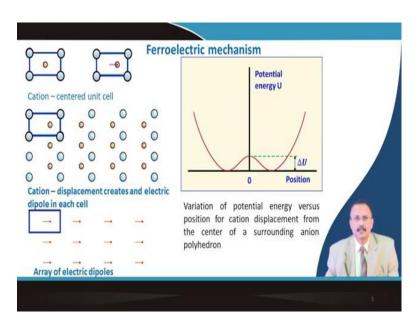


Last lecture we talked about the linear dielectric material. When you are applying an electric field the material gets polarized; as soon as the field is there, the polarization is there. Once the field is 0, then polarization also turns to be 0. Now, this particular material which we are calling ferroelectric material, they are basically non-linear dielectric.

So, their relationship between polarization and electric field is non-linear in nature. So, we will be talking about this material. Then we will talk about the hysteresis loop characteristics, which is the fingerprint of ferroelectric material and its interrelation with

domain growth. Then we will talk about the temperature dependence of this ferroelectric nature. We will introduce various types of ferroelectric materials.

And then we will introduce the concept of DC poling of this material and the doping effect to change their properties, and a special type of material which is not ferroelectric, but very similar to this, this is relaxer material is having extraordinary high dielectric permittivity. And certain applications of ferroelectric material both in their paraelectric as well as ferroelectric phase will be described.



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Now, if you see this schematic, if you have this four ions which could be anion and this small ion, which is the cation. If this is exactly at the center, then the electric lines of force of this anions and the cation, they are exactly match. So, the charge is not separated by any distance. So, distance is 0.

So, the dipole moment is 0 in this material. But under certain situation, you will find that this cation is shifted from the central position. And usually their shifts shifted because of displacive phase transition. You will see the interrelation between the phase transformation and the electronic property of these non-metallic materials, and you can correlate it now.

So, once a structural phase transition takes place that forces this cation to go somewhere else, and there the charge is not balanced. So, there is charge separated by a distance. So,

intrinsic dipole moment is there in this particular unit cell. So, we will call this is a spontaneously polarized material, because dipole moment per unit volume is nothing but polarization.

Now, once it happens that this particular cation is shifted to its right side, it has a cooperative phenomena. You see that it will actually influence all the unit cell to push this cation all in the right hand side. So, a region inside the crystal that will form where all these cations are shifted to the right hand side because of this mutual cooperative phenomena.

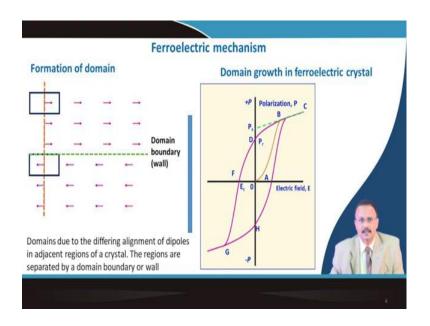
It is form a region here where the polarization direction are all identical. So, this kind of region we will term is as domain structure. So, in the domain structure, you have a array of electric dipoles which are all identically aligned. It is aligned in a particular direction. And remember there is no external electric field has been applied to this material.

So, once the polarization they are all aligned in a particular direction, so that means, there will be a creation of surface charge density. So, the electrical neutrality needs to be maintained. So, in order to maintain the electrical neutrality, there will be certain region in the same material where the polarization direction is reversed.

So, if tentatively if I assume that in a material you have only two types of this domain direction, which are basically separated by a very small distance I mean small energy barrier, so it can switch from here to here with the application of electric field right. So, this kind of material is termed as ferroelectric material.

They are spontaneously polarized, and they are having a domain structure. And this direction of the polarization is switchable from one to another by the application of a reverse electric field.

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So, the formation of domain already I have explained that this region all are in one particular direction. So, in order to maintain the charge neutrality, you have this direction where the electric dipoles are in the reverse direction. It is separated by a small boundary. We call this is a domain boundary.

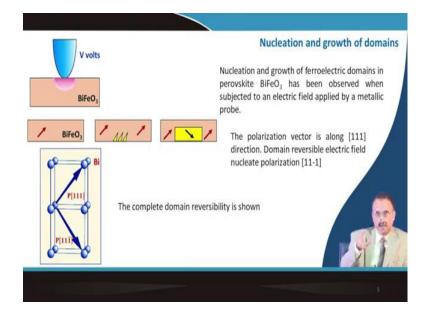
So, initially, at the virgin state when no field is applied, the polarization is 0 because certain things are this direction, certain things are in this direction, so as a whole, then it is electrically neutral. But whenever you are applying a field then according to the field direction this domain try to orient whichever is not favorably oriented.

So, at one stage at a particular field, all the domains are oriented along with the direction of the electric field. Now, once you reduce the field down to 0, then the polarization is not 0 like your linear dielectric material, but it has a remnant polarization which is denoted by the P r. And similarly at negative field direction also you have minus P r.

So, this ferroelectric material, once you apply an electric field, it is possible for you to switch the polarization direction in one direction to the other. So, the polarization is switchable, this spontaneously polarized material having switchable polarization. So, these are ferroelectric material.

There are other terms like saturation polarization, is it is the saturated value; although in this case it is not saturated as you can see. So, if it is not saturated, then you can draw a

tangent here. And wherever it cuts the y-axis that is your saturation polarization value. And this is the maximum polarization value and the field that is required to switch one polarization state to another is known as coercive field. It is denoted by E_c .



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So, this domain polarization, this can now be seen by a microscope, a piezo force microscope is used to actually see the domain and the orientation of the domain. I am not going into the details. But here is a typical example of a material which is otherwise ferroelectric and through the probe you are applying a electric field here. So, the polarization direction eventually they will all be in one particular orientation depending on the field that is being applied.

Now, once you try to reverse the polarization direction, then there will be a nucleation of the reverse domain at the bottom side of the sample. And after nucleation, it is just like nucleation and grain growth. This domain boundary will be mobile. And the polarization direction it is just opposite to this red arrow. So, it will grow, and eventually your polarization will be in the other side once you are applying a reverse electric field.

So, initially for this material, the polarization was along the body centered, body diagonal 111, and it is just reverse to 11 minus 1 direction with the application of a reverse electric field. This is for the nucleation and growth of this domain wall in this material.

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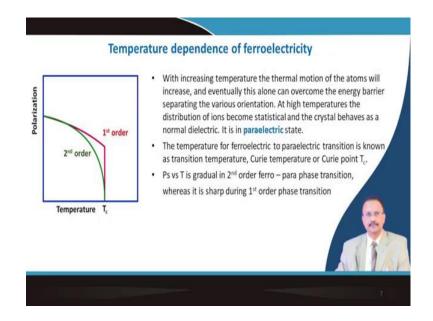


Certain material, they create a domain structure and this domain structure is actually you know that this is cancelled to each other. So, in a region all the polarization is oriented in one particular direction. But if you cross this domain boundary, then the polarization direction is such that they cancel to each other. So, the net polarization is 0. But in certain material within the unit self itself the polarization that is created, they are anti-parallel in nature.

And this type of material we call it is a anti-ferroelectric material – very limited materials exist which are antiferroelectric in nature, and lead zirconate titanate is one of them. So, it is also having a perovskite structure where Zr is within this octahedral cage, I have shown the octahedral cage here. Now, the shift of this jet cation in this octahedral cage is exactly reversed than that of the other octahedral case.

So, it is not the concept of the domain within the unit cell itself, they are anti parallelly arranged. And therefore, lead zirconate titanate they exhibits this antiferroelectric nature where the polarization in one unit cell is exactly cancelled by the polarization of the other unit cell.

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So, the materials which are ferroelectric in nature I have explained that this two different state of polarization, they are separated by a very small barrier.

Now, if you increase the temperature along with increasing the tilt, for example, so what will happen? The temperature itself will help this cation to cross this barrier and go to the other minimum energy position. So, certainly this orderedness again here also order disorder kind of transformation is coming into picture.

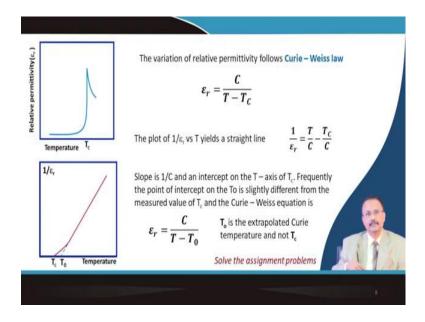
So, this orderedness will be becoming in a disorder state. So, the polarization will reduce as a function of temperature. So, at a particular temperature, you will see it is all random. So, it does not matter the polarization is in this direction or this direction.

So, it is all random. So, the material will behave like a paraelectric material. They are non-linear dielectric. Their polarization will change in a non-linear fashion with the application of electric field, but there is no spontaneous polarization left.

So, it could be a first order type, where this kind of change of polarization as a function temperature is very dramatic. It is sharp or it could be a second order type where it is gradual in nature right. So, this is a second order phase transition. And where this sharp kind of transition takes place which is first order kind of phase transition, and the temperature where it takes place it is known as Curie temperature.

So, above the Curie temperature the material behaves usually isotropically it is cubic in nature. Once you cross this temperature it there is a displacive kind of polymorphic phase transformation takes place which is displacive in nature. And then the material transform into a ferroelectric state. And it remains ferroelectric once you cool it down. There could be another phase transition involved, but that depends on a typical material.

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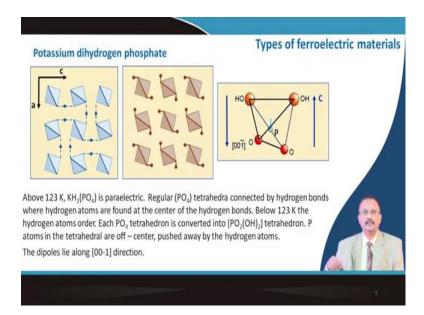


So, if you plot the dielectric constant as a function of temperature, then near the Curie temperature there is a very sharp transition as you can see here. So, this can be given by this relation that relative dielectric permittivity is dependent on Curie constant divided by T minus T C.

Here T C is the transition temperature. So, if you put T equal to T C, then your epsilon r will be undefined. So, very large dielectric constant you will get at this temperature. Below and above this temperature the dielectric constant is dramatically reduced. So, you can always reverse of the electric dielectric permittivity you can plot as a function of temperature.

So, it will be a linear plot as you can see. From the slope, you can get the curie constant and from the intercept, you can get the transition temperature. Usually the transition temperature is slightly different it is not this is a real linearity is maintained. So, the transition temperature is a bit lowered experimentally found. So, the exact temperature here is T 0. So, you can extrapolate this linear part. So, T 0 is the extrapolated Curie temperature. And this is not really the T C which is experimentally verified where the maximum the dielectric constant takes place. So, we have certain assignment problem set to clarify these issues.

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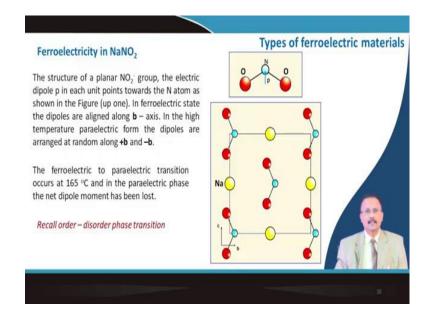


So, there are various types of ferroelectric material. The first one is related with hydrogen bonding. So, the material is potassium dihydrogen phosphate. So, the hydrogen bonds you can see this, these are the bonds of hydrogen. And the regular PO 4 kind of tetrahedra they are linked with hydrogen bond. And as such above the T C, T C is quite low here around 123 degree Kelvin. Above the T C, there is no permanent dipole, it is in the paraelectric state.

But once you cool it down below this temperature, then the hydrogen position is shifted as you can see the hydrogen is shifted towards this. So, a individual tetrahedra now here it is hydrogen is coming and sitting very close to this oxygen and very close to this oxygen for this two apex oxygen. So, due to this the P cation this phosphate P cation is shifted from its symmetric position.

So, it induced a dipole. So, dipole moment per unit volume is polarization. So, below that transition temperature, the material is spontaneously polarized, and it exhibits the ferroelectric nature. It is of limited use because as you can see it is a very low temperature where the ferroelectricity you can see.

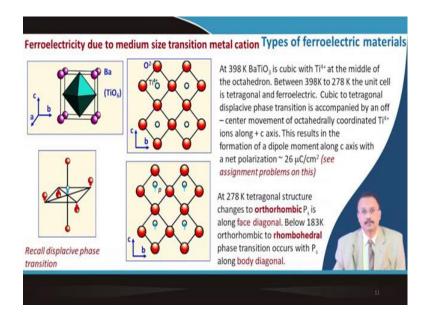
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Something similar this also I explained while I was talking about this order disorder phase transition. Sodium nitrite, here it is an arrow shaped material. And this dipole is very close to this nitrogen, nitrogen and oxygen, this bond is this dipoles are shown. So, when it is a disorder structure, then the material does not have any spontaneous polarization.

But, once it is below a certain temperature and here the Curie temperature is about 165 degree Celsius, then this is oriented in a arrowhead kind of direction is basically sodium chloride like structure where this octahedral positions are occupied by sodium and this is the nitrate ion. So, these are oriented and you get the ferroelectricity in it.

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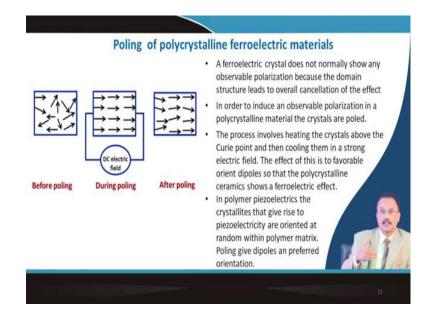
The prominent ferroelectric material is barium titanate. In cubic state, the titanium occupies this octahedral position. And once there is a phase transformation takes place at lower temperature, then the titanium position is either centrally up or it is down. So, once it is centrally up, then you do not have the matching of this two charge center. So, intrinsically the dipoles are created.

So, the creation of the dipole, that means, the polarization spontaneous polarization in this material is strongly related with this polymorphic phase transition from cubic to tetragonal state. In case of barium titanate, there are other two phase transition involved at relatively lower temperature from tetragonal, it converts to orthorhombic and from orthorhombic to rhombohedral.

So, this phase transition temperatures are not called Curie temperature. Curie temperature is only the temperature where it transform from a ferroelectric state to a paraelectric state. So, the polarization direction when cubic to tetragonal takes place that is the actual position is along z-axis.

When the other two phase transition takes place, then either it is along the phase diagonal of this FCC lattice or along the body diagonal only the polarization direction is changed.

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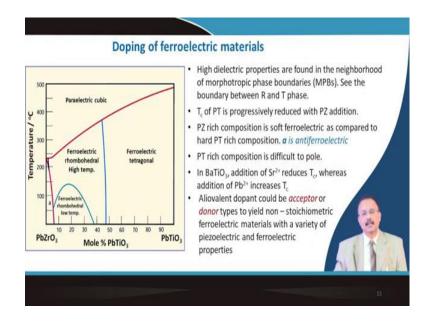


So, you can pull this material because as I said that the material is all random. So, you can increase the temperature to its respective Curie point. So, the material is so called soft. And then apply a strong electric field to orient this dipole direction to a particular direction along with the DC field direction.

And then with this field on you cool it down, so that it follows the hysteresis loop initially from the virgin state where all the dipoles are oriented in different direction. It is oriented in a particular direction, direction to the field. And then you turn on the field, and slowly cool the temperature, then it follows the reduction of the filled line and remnant polarization is there.

So, the material is polarized. And this operation is known as DC poling of the ferroelectric material.

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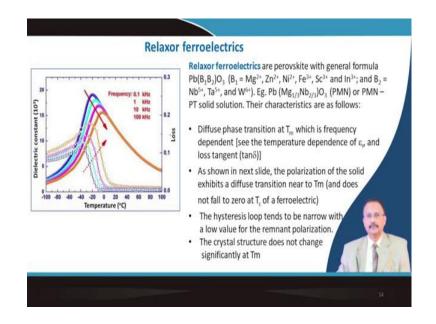
So, the property of the ferroelectric material you can increase by the cation doping and or anion doping. And you know that it creates defects inside the lattice. And how exactly it can modify the property that is beyond the scope of this lecture, but I will cite one example lead titanate is tetragonal material, and it is perfect ferroelectric. Lead zirconate is anti ferroelectric in nature.

So, you can have a solid solution of lead zirconium titanate at a particular composition about fifty-fifty. You see that both the tetragonal and the rhombohedral phase coexist. So, there are different polarization direction, 6 for tetragonal, and 8 for rhombohedral. So, there are many polarization directions available. So, material can be easily pulled.

So, along with this phase and along with this composition, which we called morphotropic phase boundary there you will find that all the property piezoelectric coefficient, ferroelectric coefficient, pyroelectric coefficient. They are all increased tremendously along with this particular composition. So, this is a MPB composition for lead zirconate titanate.

Similarly, you can play with the composition at either b site or a site of this cation introduce defect in the lattice, either it will create cation vacancy, or it will create oxygen vacancies, and that can actually influence the domain dynamics and the ferroelectric property can be grossly modified or tuned by this dopant.

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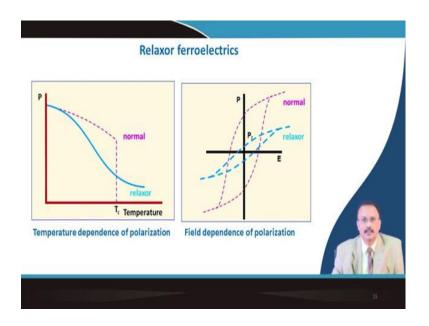
Certain ferroelectric material type material they are quite interesting and they are called relaxor material. If you see the characteristics of this material instead in the B site you have two different types of cation, in lead zirconate titanate you had zirconia and titania both are plus 4 valence.

Here intentionally we are taking two different valance state materials. For example, the two valence state material magnesium plus 2, zinc plus 2, nickel plus 2 one can take, and you can take seemingly higher valence state material like niobium which is plus 5 state, tantalum you can use, tungsten you can use. So, there is a difference in the balance state within the unit cell which are randomly oriented.

In some unit cell, you have magnesium solid cell you have niobium, so that gives a property where the dielectric constant is not a very sharp function of temperature. So, you see that there is a broad dielectric maxima that is you are getting not a sharp dielectric versus temperature curve that you are getting. Now, with the increase of the frequency, this dielectric maxima goes towards higher frequency. And with increase of the frequency, the tan delta also moves to the higher frequency range.

So, these are the characteristics of the so called relaxer material. And you can see that the dielectric constant of this material at this dielectric maxima is very high it is about 20,000 dielectric constant you are getting out of this material. So, they are special type of material, and they are not really ferroelectric in nature.

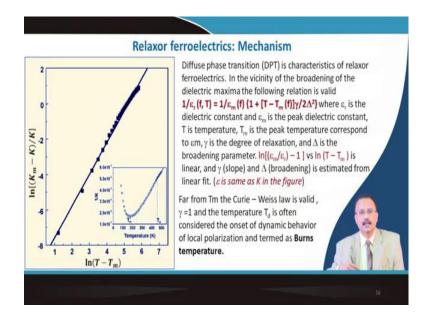
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If you see the difference here normal ferroelectric at the transition temperature, you see that there is a sharp drop of the polarization. But here you see the polarization there is no concept of this transition temperature because the phase transition does not occur. It remains in the same pseudo cubic phase.

So, you have the polarization which is continuing beyond the so called transition temperature or the maximum temperature corresponding to the dielectric maxima. And also if you cross the dielectric maxima, then the hysteresis loop is not really 0. Because what do you expect that a normal ferroelectric at T C. Beyond T C would not have any hysteresis loop, but here a slim kind of hysteresis loop in case of relaxer material also you are having.

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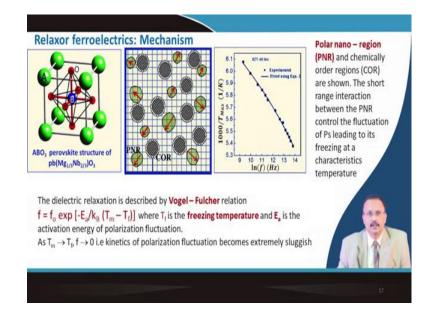


So, the mechanism is a bit complicated. And this mechanism is related to the polar nano region because of the two different charged species inside this material. So, this diffusion and this dielectric permittivity this relation is a bit complicated in this material. And I have written this relation of 1 by epsilon r.

You remember in case of the normal T C based ferroelectric material, it is epsilon r equal to C divided by T minus T C. But here if you write this inverse 1 by epsilon r, this follows this particular relation where you can see a gamma coefficient is there. And if you put gamma equal to 2, this is perfect relaxer. If this comma is equal to 1 that it translates into the normal this Curie temperature based ferroelectric material.

So, you can easily estimate the value of gamma and the broadness of this dielectric permittivity by plotting log of epsilon at maximum m divided by epsilon r minus 1 versus from this relation itself. You take log and then you plot a linear plot. And you can estimate the value of gamma, and it will take whether it is a perfect relaxer or it is in between a relaxer and ferroelectric material.

So, far from your maximum temperature may be the Curie law is valid. So, if you plot the relation for a relaxer material at very high temperature around this region which is far away from your maxima this temperature, it is valid here. And this from here you can have a specific temperature which we called the Burns temperature we can define it. So, this Burns temperature is far away from this maximum temperature where the Curie wise law is valid.

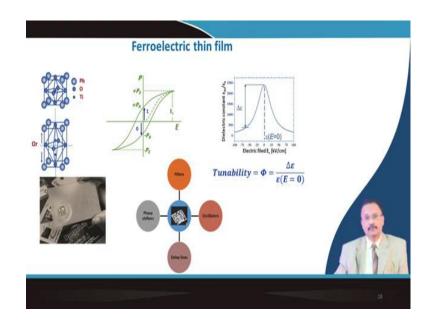


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So, it is due to a polar nano region something like this inside the otherwise matrix which is non polarizable. And this nano polar dimension, it shrinks basically when you go towards the maximum temperature region. But if you cool down the material temperature at lower temperature, they actually grows. And this frequency dependence it follows a Vogel-Fulcher kind of relationship. And I just explained it a little bit this while I was talking about the glass.

And this material shows a Vogel-Fulcher relationship, and you can actually get the freezing temperature where this kind of fluctuation of the polarization is grossly minimized and material behaves like a normal ferroelectric material. But if you increase the temperature very close to the maximum T m value, then it switches so fast that it really is in between a direct polarizable I mean spontaneous polarized material, and a paraelectric material. It is in between that stage.

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So, the ferroelectric thin film relaxer and ferroelectric in its paraelectric region they are a industrially very lucrative material. And relaxer ferroelectrics is mainly used for those places where high energy density is required because it has a very large star storage capacity. Normal ferroelectric material if you thin down the thickness, then it can be switched within 5 volt.

So, that therefore, in thin film state you can make lot of device. One such interesting device is a non-volatile memory where unlike the dynamic random access memory, you can store digital 1 and digital 0 in a matrix of the ferroelectric thin film memory. And digital 1 and 0 can be stored it can be switched very fast. So, very fast non-volatile memory device can be made.

But unfortunately the problem of fatigue because the polarization changes with number of read and write cycle that has not yet been overcome. So, it has not come into the market in a very big way. But in paraelectric state the tunability that is the change in the dielectric constant with the electric field that is an important parameter which can define various types of device like filter, oscillators, phase shifters, or delay lines, they are very very much lucrative for microwave communication.

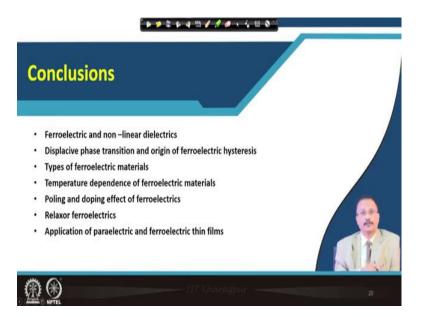
So, this material or microwave dielectric material, which is having a transition temperature near room temperature. So, slightly above room temperature, they behave like a paraelectric material there is no hysteresis, but the dielectric is tunable, and this materials are very lucrative for communication kind of devices.

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So, this study material is the book by Tilley and also Barsoum the relevant chapters. And for a in depth study, you can consider the books by Lines and Glass and Moulson, or a very original book by J.C Burfoot.

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So, we have talked about ferroelectric and non-linear dielectric material, displacive phase transition is the origin of the ferroelectric hysteresis, type of the ferroelectric material we

have defined, then temperature dependence of the ferroelectric material pulling concept and use of the aliovalent dopants in controlling the ferroelectric properties. Then we have introduced the relaxer materials having very high dielectric permittivity.

And very brief overview of ferroelectric material in its ferroelectric state and in its paraelectric state in thin film form has been explained.

Thank you so much for your attention.